

Biological signals in clumped isotopes of brachiopod shells

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Clumped isotopes offer the potential to unlock the rich environmental and biological record within marine carbonate biominerals. The co-occurrence, or ‘clumping’, at thermodynamic equilibrium, of two heavy isotopes, such as ¹³C and ¹⁸O, in carbonate molecules, records only temperature [e.g. Eiler, 2007; Eiler, 2011; Schauble *et al.*, 2006]. Brachiopods have a long continuous fossil record of stable low-Mg calcite shells [Parkinson *et al.*, 2005]. Since brachiopod primary (outer) and secondary (inner) shell layers form at the same temperature they would be predicted to have the same degree of clumping. We show that in examples of two brachiopod species, *Neothyris lenticularis* and *Laqueus rubellus*, there are biological signals in the clumped isotopes.

Temperatures calculated from measured $\delta^{18}\text{O}$ and known $\delta^{18}\text{O}$ of the seawater from which the brachiopods were collected, using the equation of Parkinson *et al.* [2005], are within the measured temperature range of the seawater from which they were collected. Temperatures calculated from clumped isotope Δ_{47} values, using the calibration of Henkes *et al.* [2013], are well above the measured temperature of the seawater from which they were collected. These higher temperatures reflect higher Δ_{47} values and therefore a lesser degree of clumping.

Primary and, particularly, secondary layers are “anticlumped” with less clumping than expected. Biomineral formation is controlled by enzymes that may prevent the attainment of thermodynamic equilibrium and thus influence the extent of clumping. Understanding these biological signatures in clumped isotopes, and determining the extent to which they are widespread among biominerals, offers an incisive tool to investigate biomineralisation.

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